Direct Observation of the Kinetically Relevant Site of CO Hydrogenation on Supported Ru Catalyst at 700 K by Time-Resolved FT-IR Spectroscopy

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Abstract

Time-resolved FT-IR spectra of carbon monoxide hydrogenation over alumina-supported ruthenium particles were recorded on the millisecond time scale at 700 K using pulsed release of CO and a continuous flow of H_2/N_2 (ratio 0.067 or 0.15, 1 atm total pressure). Adsorbed carbon monoxide was detected along with gas phase products methane (3016 and 1306 cm^{-1}), water (1900 – 1300 cm^{-1}), and carbon dioxide (2348 cm^{-1}). Aside from adsorbed CO, no other surface species were observed. The rate of formation of methane is 2.5 ± 0.4 s^{-1} and coincides with the rate of carbon dioxide growth (3.4 ± 0.6 s^{-1}), thus indicating that CH_4 and CO_2 originate from a common intermediate. The broad band of adsorbed carbon monoxide has a maximum at 2010 cm^{-1} at early times (36 ms) that shifts gradually to 1960 cm^{-1} over a period of 3 s as a result of the decreasing surface concentration of CO. Kinetic analysis of the adsorbed carbon monoxide reveals that surface sites absorbing at the high frequency end of the infrared band are temporally linked to gas phase product growth. Specifically, a (linear) CO site at 2026 cm^{-1} decays with a rate constant of 2.9 $\pm$ 0.1 s^{-1}, which coincides with the rise constant of CH_4. This demonstrates that the linear CO site at 2026 cm^{-1} is the kinetically most relevant one for the rate-determining CO dissociation step under reaction conditions at 700 K.

1. Introduction

Supported Ru catalysts are among the most active for the hydrogenation of CO to methane.[1,2] In situ infrared spectroscopy has played an important role in establishing mechanistic aspects of CO hydrogenation over metal catalysts.[3-5] In particular, monitoring of the infrared band of adsorbed carbon monoxide while simultaneously recording gas phase products by mass spectrometry revealed that dissociation of the CO molecules to surface C and O species is the rate limiting step, while the hydrogenation steps of carbon species leading to CH_4 are fast by comparison according to most studies.[6-9] Moreover, the infrared method has allowed identification of distinct modes of surface adsorption of (undissociated) CO, namely linear (Ru-CO, 2047-1960 cm^{-1})[9-12], bridge-bonded (Ru_2-CO, 1950-1900 cm^{-1})[9,10], and μ-bonded species (Ru-CO-Ru, 1750 cm^{-1} or Ru-CO-Al(support), 1700-1500 cm^{-1})[9,13]. Linear CO was found to exhibit the fastest hydrogenation rate.[6-9] However, even pulsed methods[7] or step (reactant switch) methods[8] with a time-resolution of a few seconds are unable to demonstrate the relative kinetic importance of specific CO surface sites under typical reaction conditions. In order to determine the sites most relevant for CO methanation over Ru catalyst, time-resolved monitoring of the decay of CO surface species and the concurrent growth of hydrogenation product(s) on the time scale of milliseconds or faster is required.

In this paper, we report a time-resolved rapid-scan FT-IR study of CO hydrogenation over Al_2O_3 supported Ru particle catalyst at a reaction temperature of 700 K. The experiments revealed the site of adsorbed CO that exhibits the highest activity. A direct

temporal link between the decay of the CO surface site and the final product rise is demonstrated.

2. Experimental Section

Time-resolved FT-IR spectra were recorded in the rapid-scan mode on a Bruker model IFS88 spectrometer equipped with a HgCdTe PV detector Kolmar Technologies model KMPV8-1-J2 (8 micron bandgap) or a HgCdTe PV detector model KMPV11-1-J2 (12 micron bandgap) as described previously.[14,15] The method is described briefly below. The mirror velocity was 160 kHz, and the spectral resolution was 4 cm^{-1}. The protocol for obtaining the transient spectra consisted of the recording of 99 interferograms (double-sided/forward-backward) following a carbon monoxide pulse, corresponding to 396 single-sided interferograms. Single beam spectra obtained from the interferograms consisted of four 50 ms time slices followed by three 100 ms time slices, then a 10900 ms time slice, and the last time slice was 900 ms. A total of 50 such sets of single beam spectra generated by 50 carbon monoxide pulses were stored as the result of one experiment. Final time-resolved spectra for a given time delay were obtained by calculating the ratio of each of the 50 corresponding stored single beam spectra against the single beam spectrum taken just before the pulse. The 50 ratioed spectra were then averaged to yield the absorbance time slice for a given time delay. The results of 10 such experiments were averaged for further S/N improvement. Spectral deconvolution was preformed with GRAMS/AI software Version 7.02, Thermo Electron (Gaussian bands, Levenburg-Marquardt method).

Time-resolved runs on the slower time scale of seconds were conducted by again recording 396 interferograms following a carbon monoxide pulse (double-sided/forward-backward at 160 KHz and 4 cm^{-1} resolution), but this time dividing the 99 interferograms into 10 "buffers" at varying time duration. Each buffer contains the average of a pre-selected number of consecutive interferograms. The first two buffers were of 256 ms duration (averaging 8 interferograms) followed by three buffers of 640 ms duration (20 interferograms), one buffer of 1280 ms length (40 interferograms), one of 1920 ms length (60 interferograms), one of 2560 ms length (80 interferograms), one of 3840 ms length (100 interferograms), and the last buffer was of 1280 ms duration (40 interferograms). Hence, the data stored after each carbon monoxide pulse consisted of 10 averaged interferograms taken at 128, 384, 832, 1472, 2112, 3072, 4672, 6912, 9792, 12032 ms after onset of the reactant pulse (time indicates midpoint of buffer).

The Al_2O_3-supported Ru catalyst (Aldrich, 5% Ru, Degussa type H213 R/D, BET surface area 96 m^2g^{-1}) was prepared in the form of a pressed wafer with an embedded W grid. The latter is made of a 0.49 in. diameter tungsten foil (thickness 0.002 in.) featuring laser-drilled 0.012 in. holes. The grid, which was held by a Ni jaw similar to a design described by Yates[16] was electrically heated and the temperature monitored by a thermocouple mounted on the W grid. The catalyst was situated in the center of home built 100 cm^3 stainless steel reactor cell equipped with two flange-mounted BaF_2 windows for transmission infrared spectroscopy. The catalyst was transparent in the region 5000-800 cm^{-1} (reduced sensitivity below 1100 cm^{-1} because of Al-O stretch

absorptions). The continuous flow of a H_2/N_2 mixture (ratio 0.067 or 0.15) with a flow of either 4.5 L/min or 5.4 L/min at a total pressure 1 atm entered the cell through a ¼ in. tube on one side and exited through an exhaust line on the other. The flow of each gas was regulated by MFC valves (MKS Instruments). Millisecond time resolution was achieved by the synchronization of carbon monoxide pulses of 30 ms duration with the forward motion of the interferometer mirror.[15] The spacing between carbon monoxide pulses was 12.8 s, which assured that all reaction had ceased prior to arrival of a fresh pulse. The pulses were released through a fast value (General Valve Series 99 pulsed valve coupled with an Iota One pulse driver) and contained 15 μmol carbon monoxide. The pulses merged with the continuous H_2/N_2 flow 7 cm upstream from the center of the reactor cell, resulting in arrival of the CO pulse in the catalyst zone within a few ms after opening of the valve. Before each series of experiments, the Ru/Al_2O_3 catalyst was exposed for six hours to a H_2/N_2 flow at 600 K and then for one hour at 700 K in order to assure complete reduction of the Ru surface. Carbon Monoxide (Air Gas, 99.99%), hydrogen (Air Gas, 99.9999%), hydrogen in nitrogen (Airgas, H_2/N_2 ratio 0.15), deuterium (Isotec, 99.8 % D), and nitrogen (Air Gas, 99.9995%) gas were used as received.

3. Results and Discussion

The transient spectra observed following initiation of catalysis over Ru/Al_2O_3 catalyst at 700 K with a carbon monoxide pulse are displayed in Figure 1. The bottom trace is the

first spectrum observed, with its midpoint delayed by 36 ms relative to the opening of the pulsed carbon monoxide valve. Subsequent traces are shown at 95, 223, 577, and 6000 ms. The temporal resolution of the first three traces is 50 ms, the fourth is 100 ms, and the fifth was recorded over several seconds. The most prominent band is due to gas phase carbon monoxide, centered at 2143 cm^{-1}.[17] As shown in Figure 2, gaseous CO decreases principally due to removal of the reactant from the infrared viewing zone by rapid gas flow.[18,19]

In addition to gas phase carbon monoxide, bands are observed at 3016, 2348, 2010, and 1306 cm^{-1} (Figure 1). The most intense of these absorptions (2010 cm^{-1}) is unsymmetrical and very broad, with a tail extending to about 1500 cm^{-1}. This band is assigned to adsorbed carbon monoxide based on previous infrared studies.[3,4,6,9,13,20-24] The other bands, shown on an expanded scale in Figures 3 and 4 are due to gas phase products methane (Q branch peaks at 3016 cm^{-1} (ν_3) and 1306 cm^{-1} (ν_4))[25] and carbon dioxide (2348 cm^{-1})[26]. For experiments using D_2, the corresponding CD_4 gas phase bands with Q branches at 2256 cm^{-1} (ν_3) and 993 cm^{-1} (ν_4) were observed.[25] In addition, a series of sharp bands are noted in the 1900 – 1300 cm^{-1} region (Figure 3, panel b). These are assigned to the spectrum of gaseous H_2O. Faithful recording of infrared ro-vibrational bands of this and the other gaseous products would require much higher spectral resolution than available in the time-resolved mode (the limiting factor is the file size of the very large time-resolved interferogram stacks that the data acquisition electronics must handle. Furthermore, higher spectral resolution can only be achieved at the expense of time resolution because of the longer mirror path). As a result, peak intensities of ro-

vibrational bands of the time-resolved spectra are smaller than of static spectra recorded at appropriate resolution. Aside from the species mentioned above, no other bands are present in any of the transient spectra.

The adsorbed carbon monoxide band is most intense in the first spectrum recorded just after initiation of catalysis, and then decreases with time. This decrease is accompanied by a red shift from 2010 cm^{-1} at 36 ms to 1990 cm^{-1} at 897 ms, as shown in Figure 5. In addition, the band broadens, especially around the peak position. As can be seen from Figure 6, the red shift of the band continues on the time scale of seconds. The final peak position is reached after 3 s and lies at 1960 cm^{-1}. Frequency and behavior of this band agree with that of linear Ru-CO species.[4,8,13,21] The red shift is consistent with the gradual reduction of dipole coupling among neighboring linear CO species as the surface concentration of the reactant diminishes by reaction with hydrogen.[9,22,27] It is important to note that after 7 s (6912 ms trace of Figure 6) the band of adsorbed CO has completely vanished, confirming that reaction ceases before a fresh CO gas pulse reaches the catalyst again.

In order to gain more detailed insight into the red shift and broadening of the adsorbed carbon monoxide band, the kinetics were examined by two different methods. The first consisted of determining the integrated absorbance of the entire band with peak absorbance near 2010 cm^{-1} (integration from 2050 cm^{-1} to 1650 cm^{-1}). The intensity was found to decay with a rate constant of 0.45 ± 0.03 s^{-1}, as shown in Figure 7. It agrees within a factor of 2 with the rate with which gaseous CO is removed from the catalyst

zone by gas flow. Given the systematic error associated with the determination of the gas phase band intensity because of insufficient spectral resolution (see above), we consider the two rates as the same. This suggests that a steady state distribution between gas phase and surface adsorbed CO is established on the time scale of seconds. Fast exchange of CO between Ru surface and gas phase has been observed by previous authors.[8] The second method only considers the portion of the adsorbed CO band that corresponds to the bleach at early times (< 1 s). As can be seen from the difference spectra in Figure 8, the bleach remains centered at 2026 cm^{-1} for the first 600 ms of the reaction. Therefore, a spectral deconvolution of the profile of adsorbed CO was conducted with one Gaussian component fixed at 2026 cm^{-1} (GRAMS/AI software). The result of deconvolution and the kinetics of the decay are displayed in Figure 9. The calculated best fit to a single exponential function gives a rate constant of 2.9 ± 0.1 s^{-1} (0.067 H_2/N_2 ratio, 4.5 L/min flow). Note that the 2026 cm^{-1} site is replenished upon arrival of the next CO reactant pulse, which allowed us to repeat the recording of the time resolved spectra for signal to noise improvement, as described in the Experimental Section.

Determination of the kinetics of the gas phase products, CH_4 and CO_2, required that the data be fit using an equation that describes both the rise of the product and the decay due to the loss by removal through rapid gas flow. These processes can be described by a model consisting of two consecutive steps R → P → P', where R is carbon monoxide, P is gas phase product in the IR viewing zone, and P' is gas phase product after it has been removed from viewing zone by gas flow. The corresponding differential and integrated equations are:[28]

$$R \xrightarrow{k_1} P \xrightarrow{k_2} P' \quad (1)$$

$$\frac{d[P]}{dt} = k_1[R] - k_2[P] \quad (2)$$

$$A^P = A \frac{k_1}{k_2 - k_1} \left(\exp(-k_1 t) - \exp(-k_2 t) \right) \quad (3)$$

(A^P, absorbance of product P at time t; A, asymptotic absorbance of P'). The corresponding fits for the kinetic behavior of methane and carbon dioxide are shown in Figure 10(a) and (b), respectively. The growth rate of the two methane bands at 3016 and 1306 cm^{-1} was found to be the same, with $k_1 = 2.5 \pm 0.4$ s^{-1} (0.067 H_2/N_2 ratio, 4.5 L/min flow). The rate of growth (k_1) for carbon dioxide under identical H_2 concentration and flow conditions is 3.4 ± 0.6 s^{-1}, which is the same rate within uncertainties that was found for methane. We conclude that these two products, which have a branching ratio of 0.44 originate from the same intermediates, namely surface C and surface O species. Moreover, we find that the decay of the 2026 cm^{-1} site of linear Ru-CO agrees with the rate of rise of the products, indicating that this is the kinetically relevant site of CO for reaction at 700 K. The fact that the highest frequency component of linear surface CO is the kinetically most relevant species agrees with the expectation that the most weakly bound CO reactants are the most reactive.[29] The rate k_2 determined for the decay of methane (0.52 ± 0.08 s^{-1}) and carbon dioxide (1.2 ± 0.2 s^{-1}) lie within a factor of 2 of the rate determined for the removal of gas phase carbon monoxide (see Figure 2). In light of the systematic errors associates with infrared intensity measurements of narrow gas phase absorptions, we consider these rate constants in agreement.

It is important to add that the methane rise does not exhibit any delay (induction period) and follows a first order law even though arrival of the CO reactant pulse is expected to displace surface adsorbed hydrogen (the heat of adsorption of CO on Ru exceeds that of hydrogen by more than a factor of two (CO on Ru(001), 36 kcal mol^{-1}; hydrogen on Ru(001), 15 kcal mol^{-1}).[30,31] Our observation is consistent with previous reports which showed that the steady state hydrogenation rate of CO over Ru surfaces is fairly constant due to the fact that the hydrogen coverage remains high even in the presence of near monolayer CO coverage.[6] This was explained by the fact that the competition between CO and hydrogen is limited to certain sites.[6,32,33] In our time-resolved experiments, the Ru particles are exposed to a continuous flow of H_2 and the metal surface is adequately covered with hydrogen before a fresh CO pulse arrives.

According to the spectral traces of Figure 8, depletion of the red shifted linear, bridge-bonded and μ-bonded CO sites is slow on the sub-second time scale. Since a fast steady state distribution is established between adsorbed and gas phase CO, with the latter swept from the catalyst zone within a 5 s, depletion of these sites probably occurs mainly by desorption rather than reaction. Carbon monoxide desorption may be aided by displacement by H from the continuous H_2/N_2 flow, as has previously been observed for CO adsorbed on several metal surfaces.[34,35]

While quantitative analysis of the kinetic behavior of the H_2O product was not possible because of the lack of spectral resolution, our observation of growth on the

hundreds of ms time scale is in agreement with previous reports of efficient reaction of surface O with hydrogen to form H_2O upon CO hydrogenation over Ru surfaces.[4,8,20]

4. Conclusions

Time-resolved FT-IR spectroscopy has revealed a sharp absorption band at 2026 cm^{-1} as the kinetically relevant surface site of linear CO for hydrogenation on alumina-supported Ru particles at 700 K. A direct temporal link exists between the decay of the CO site (2.9 ± 0.1 s^{-1}) and the rise of gaseous CH_4 and CO_2, which confirms that these products share the rate-limiting step of dissociation of carbon monoxide to surface C and O species. The lack of observation of transient CH_x surface intermediates is consistent with hydrogenation steps occurring fast on the time scale of CO dissociation. Reaction of surface O with CO competes with capture by hydrogen to form H_2O. This is the first direct observation of a specific metal surface site that is kinetically relevant for CO hydrogenation under reaction conditions at high temperature. The more strongly held linear, bridge or μ-bonded surface CO species absorbing in the range 2000-1500 cm^{-1} react on the time scale of several seconds or longer, a time regime that is dominated by the removal of the reactants from the catalyst zone by gas flow. While the interpretation of the experiments reported here is limited by the absence of a steady surface coverage of the catalyst by CO, a further improvement of the mechanistic understanding based on such time-resolved experiments could be achieved by running the parent $^{12}CO + H_2$ catalysis continuously while delivering ^{13}CO ms gas pulses for monitoring of transient species. Such experiments are planned.

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Figure Captions

Figure 1. Rapid-scan survey spectra of CO + H_2 reaction induced by a carbon monoxide pulse over Ru/Al_2O_3 at 700 K recorded at 50 ms resolution (H_2/N_2 = 0.15). Times refer to the time delay between the opening of the pulsed valve and the midpoint of the corresponding interferogram slice. Gas phase carbon monoxide is CO(g) and adsorbed carbon monoxide is CO(a).

Figure 2. Decrease of carbon monoxide absorption (peak intensity of the 2175 cm^{-1} band) caused by gas flow (H_2/N_2 = 0.067). The solid line represents a best fit using a single exponential function.

Figure 3. Rapid-scan spectra in the (a) 3200-2800 cm^{-1} and (b) 1800-800 cm^{-1} regions observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.15). The bottom trace shows the static spectrum of an authentic methane sample recorded with the same spectral parameters used for the time-resolved CO + H_2 runs.

Figure 4. Rapid-scan spectra in the 2625-2250 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.15). The bottom trace shows the static spectrum of an authentic carbon dioxide sample recorded with the same spectral parameters used for the time-resolved CO + H_2 runs.

Figure 5. Rapid-scan spectra in the 2500-1500 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K during the first 1000 ms (H_2/N_2 = 0.067). Gas phase bands due to carbon monoxide have been subtracted.

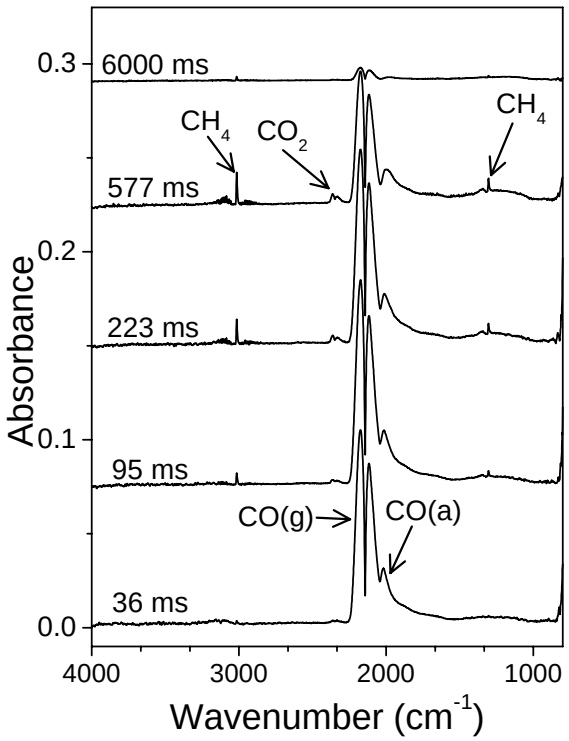
Figure 6. Rapid-scan spectra in the 2800-1200 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067) showing the decay of adsorbed carbon monoxide in the time range 1000 ms to 8000 ms. The range 2220 to 2060 cm^{-1} of intense gaseous CO absorption is not shown.

Figure 7. Kinetics of the adsorbed carbon monoxide observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). Integrated area between 2050 cm^{-1} and 1650 cm^{-1} was used.

Figure 8. Infrared difference spectra (time t – 36 ms) reveal the bleach at 2026 cm^{-1} due to reaction of adsorbed carbon monoxide (H_2/N_2 = 0.15). The 36 ms trace following initiation of CO + H_2 catalysis at 700 K is also displayed. The gas phase CO band has been subtracted.

Figure 9. Kinetics of adsorbed carbon monoxide (integrated area of 2026 cm^{-1} band) observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). The solid line represents a best fit using a single exponential function. The inset shows the component bands resulting from spectral deconvolution of the 36 ms trace.

Figure 10. Kinetics observed for gas phase products (a) methane (peak absorbance at 3016 cm^{-1}) and (b) carbon dioxide (peak absorbance at 2363 cm^{-1}) following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). Solid lines represent best fits using eq. (3).



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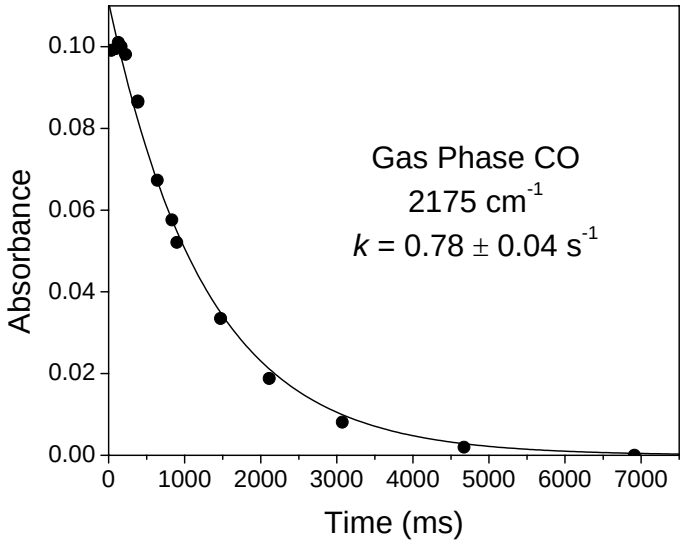

Figure 2. Decrease of carbon monoxide absorption (peak intensity of the 2175 cm^{-1} band) caused by gas flow ($H_2/N_2 = 0.067$). The solid line represents a best fit using a single exponential function.

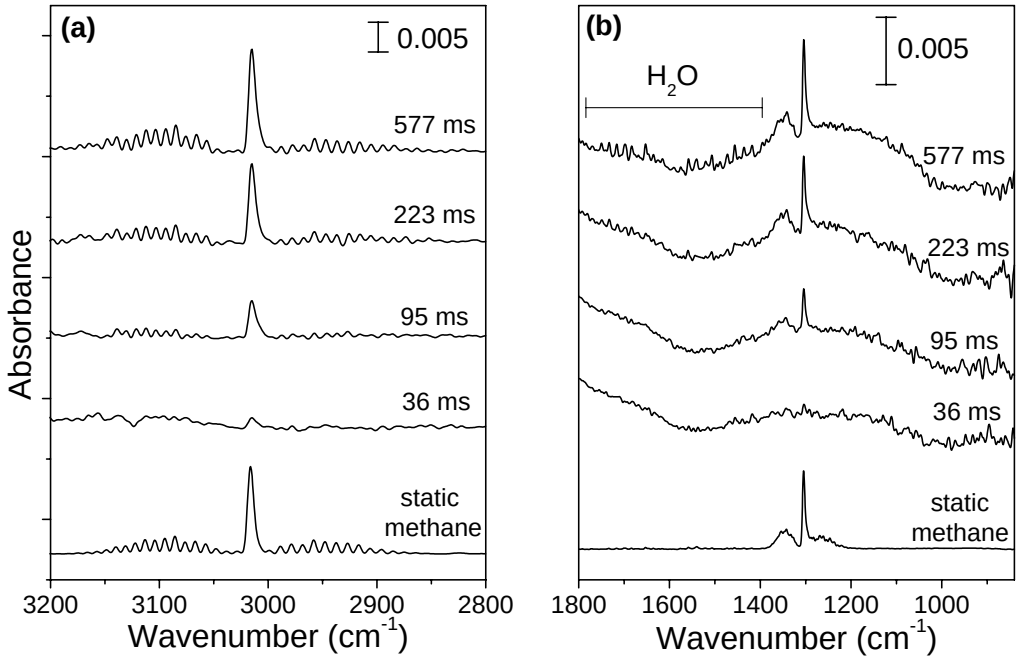

Figure 3. Rapid-scan spectra in the (a) 3200-2800 cm^{-1} and (b) 1800-800 cm^{-1} regions observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.15). The bottom trace shows the static spectrum of an authentic methane sample recorded with the same spectral parameters used for the time-resolved CO + H_2 runs.

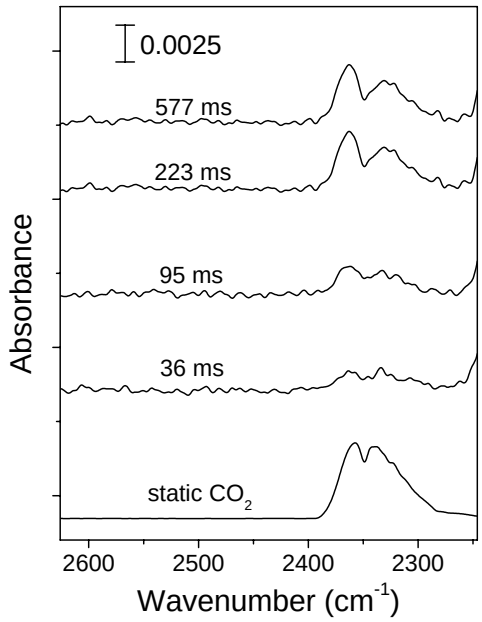

Figure 4. Rapid-scan spectra in the 2625-2250 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.15). The bottom trace shows the static spectrum of an authentic carbon dioxide sample recorded with the same spectral parameters used for the time-resolved CO + H_2 runs.

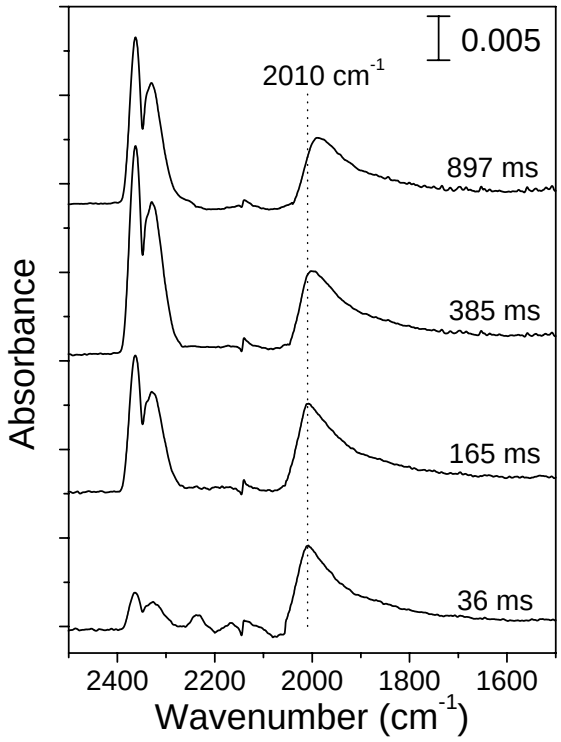

Figure 5. Rapid-scan spectra in the 2500-1500 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K during the first 1000 ms (H_2/N_2 = 0.067). Gas phase bands due to carbon monoxide have been subtracted.

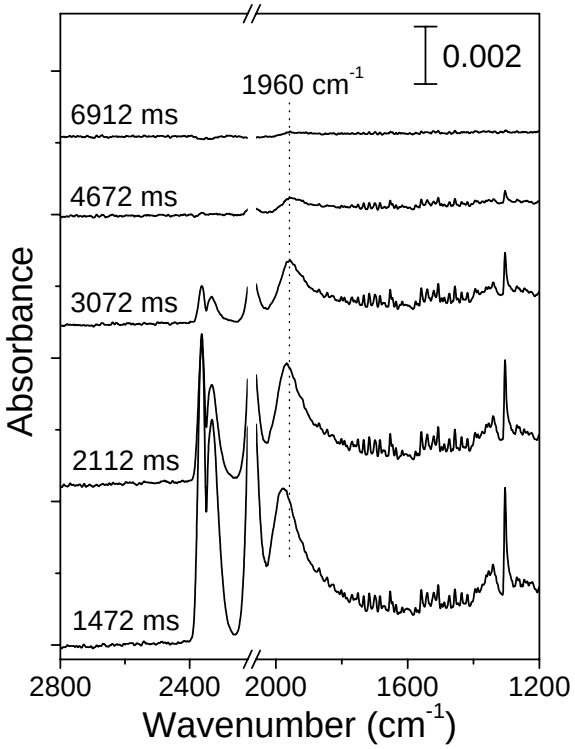

Figure 6. Rapid-scan spectra in the 2800-1200 cm^{-1} region observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067) showing the decay of adsorbed carbon monoxide in the time range 1000 ms to 8000 ms. The range 2220 to 2060 cm^{-1} of intense gaseous CO absorption is not shown.

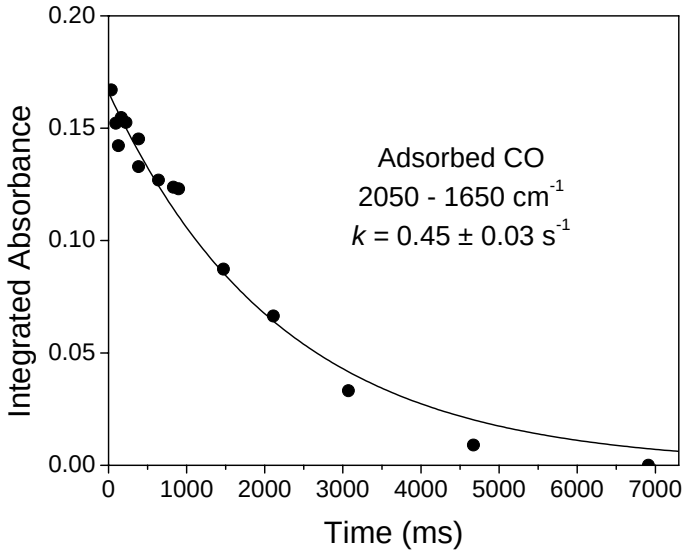

Figure 7. Kinetics of the adsorbed carbon monoxide observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). Integrated area between 2050 cm^{-1} and 1650 cm^{-1} was used.

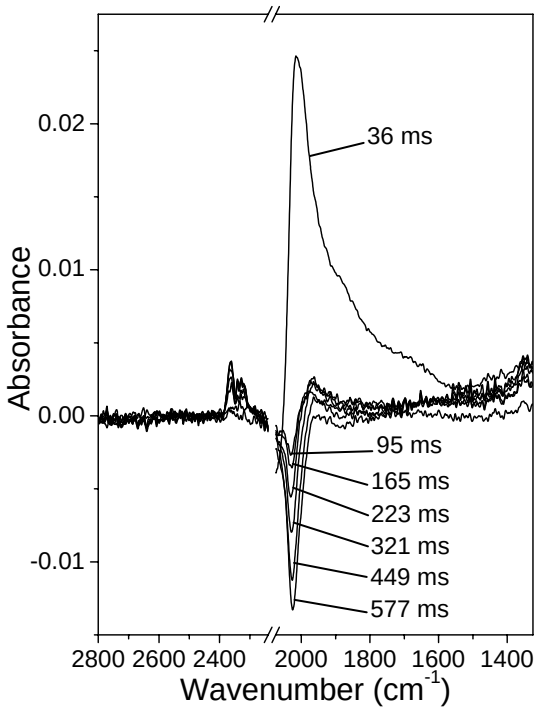

Figure 8. Infrared difference spectra (time t – 36 ms) reveal the bleach at 2026 cm^{-1} due to reaction of adsorbed carbon monoxide (H_2/N_2 = 0.15). The 36 ms trace following initiation of CO + H_2 catalysis at 700 K is also displayed. The gas phase CO band has been subtracted.

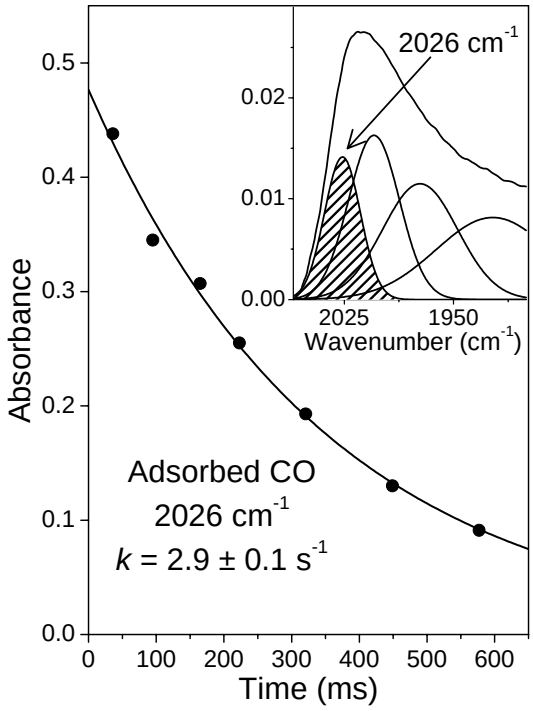

Figure 9. Kinetics of adsorbed carbon monoxide (integrated area of 2026 cm^{-1} band) observed following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). The solid line represents a best fit using a single exponential function. The inset shows the component bands resulting from spectral deconvolution of the 36 ms trace.

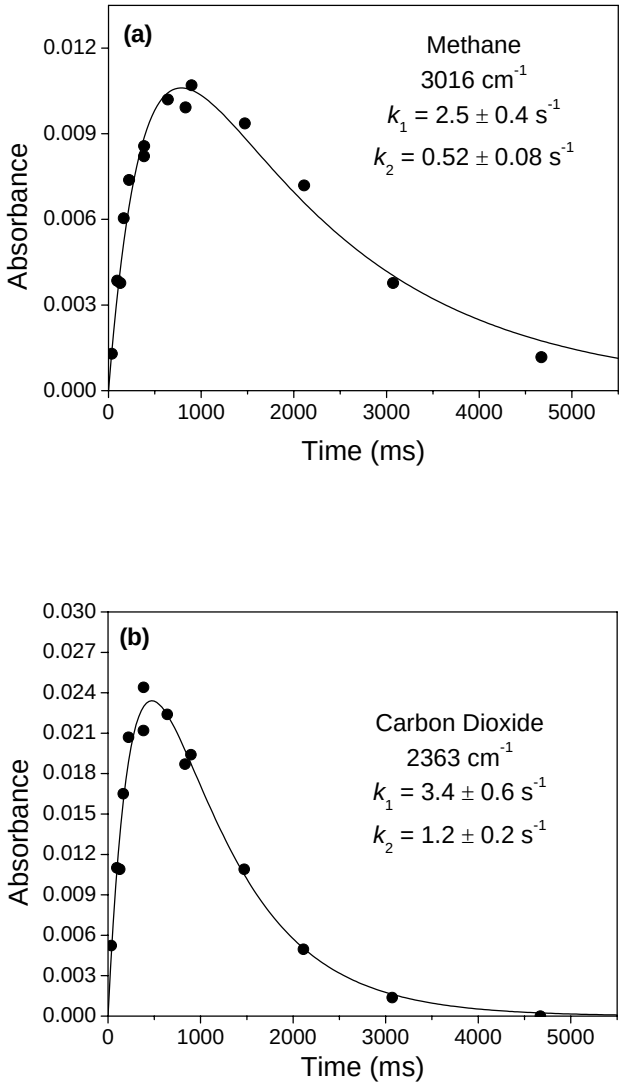

Figure 10. Kinetics observed for gas phase products (a) methane (peak absorbance at 3016 cm^{-1}) and (b) carbon dioxide (peak absorbance at 2363 cm^{-1}) following initiation of CO + H_2 catalysis at 700 K (H_2/N_2 = 0.067). Solid lines represent best fits using eq. (3).